Optical Properties of PVC Composite Modified During Light Exposure to Give High Absorption Enhancement

Rasheed N. Abed[1*], Emad Yousif[2#], Abdul Rahman N. Abed[1], Alaa A. Rashad[2],
Abas Hadawey[3], Ali H. Jawad[4]
[1]Mechanical Engineering Department, Engineering College, Al-Nahrain University, 64040, Baghdad, Iraq.
[2]Department of Chemistry, College of Science, Al-Nahrain University, 64021, Baghdad, Iraq.
[3]School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, United Kingdom
[4]Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam 40450, Selangor, Malaysiana
*rasheed.n.abed@nahrainuniv.edu.iq , #emadayousif@gmail.com

Abstract

Modified poly (vinyl chloride) (PVC) films have been synthesized with a simple superficial deposition by using solvent tetrahydrofuran (THF). These modified films were prepared by a casting method over a glass substrate. Different types of the amino group with a suitable aromatic aldehyde as an organic compound, which were reacted to prepare different PVC composite films. These films have been analyzed by UV-Visible spectra. The percentage of PVC was (0.25 g) with (0.05 g) amino group and aromatic aldehyde combinedly, then dissolved with (8 ml) of tetrahydrofuran (THF) at room temperature (300 K). The optical properties as absorption coefficient, reflectance, transmittance, skin depth, energy gap, refractive index, extinction coefficient, and urbach energy were studied. The transmittance value of the pure PVC film was 1.0 then declined gradually after dispersion with the compounds to the lowest value at 0.1, the reflectance also decreased. The energy gap for direct allowed decreased from (5.1 to 2.9 eV), and indirect transition decreased also from (5.0 to 2.8 eV), this behavior indicate that the modified films become work as semi-crystalline compounds toward the light. In tailoring, the optical properties, and urbach energy have been increased after mixed with PVC polymer. The scattering energy $(\boldsymbol{E_d})$ and the effective single oscillator $(\boldsymbol{E_o})$, were decreased. In a similar manner the dielectric constant high frequency (ε_∞) and effective mass $\left(\frac{\boldsymbol{N}}{\boldsymbol{m^*}}\right)$, of dielectric constants were increased for PVC modified films. The PVC modified films are appropriate for anti-reflected coating while being good suitable in high refractive lenses and photovoltaic cells applications.

Keywords: PVC modified films, Optical properties, surface morphology, Urbach energy, dielectric constant high frequency.

1.Introduction

The organic compounds are promising as a solar exporter property for a low cost when technological modifications carried out on them; they are a low-cost coating layer. Solar energy exporter is very significant in sustainable energy. Although organic matters have a cheap cost, getting easily, and are deemed essential in commercial utilize due to their efficiency in global sources of energy [1]. These organic compounds may be transacted as a photoconductive of solar energy photons enter inside the coating and absorbed through the electrons which occupy the orbital of the organic compounds and transferred to the lower unpreoccupied orbital to produce a pair of holes to generate the carriers that create the conductivity [2-4].

Poly (vinyl chloride) PVC has a lower thermal conductance and high resistivity; therefore, after reinforcing PVC with organic compounds, the conductance properties will be improved. The modified PVC surface improve the optical properties; this improvement occurred due to the reaction of the organic compounds with the PVC chain to enhance the absorption of the incident light through the surface coating.

The present work differs from other researchers who work on embedding nano-materials in the PVC polymer. In this research paper have been utilized the organic compounds to modify PVC and improve the optical properties. There is little information that appears about the effect of the organic compounds on peculiarity of polymer PVC. Furthermore, there are some researchers which state how to modify PVC by using a group of compounds such as, phthaloyl groups and thiadiazol were used to modify PVC, which they are completely differs from the present work.

The modified composites have been synthesized by embedded these groups in the PVC lattice to chelate them inside the structure, and the energy gap of the modified PVC was computed. From the analysis of the results it is reveal the behavior of the energy gap ascends with the modified polymer [4, 5]. Further, PVC compounds were modified by Schiff base and (1-4) triazole-3-thiol with copper (II) to grant the resulting compounds the ability to endure the UV wavelength for an extended period of irradiation, these units of aromatic heterocyclic connected with the backbone PVC lattice to promote the photo stabilization through the surface coating for the modified PVC compounds [6]. Regarding, the amino group with an appropriate aromatic aldehyde were utilized to modify PVC by shifting halogen and reaction with PVC lattice to strengthen the photostability of compounds by entered them through the moieties of the structure [7, 53]. In addition, the chains of polymer PVC modified by a Schiff base are grafted to gain a pliable PVC and give a homogenous polymer compound, which is generated by combining a copper chloride (CuII) with the PVC compound to give PVC-L-Cu (II). This PVC compound film was exposed to irradiation under (300 h) to grant them photo stabilization through the environmental effect [8]. To some extent, not completely, the films of PVC modified by a Schiff base with inserted a nickel chloride to the structure of the compounds to be a homopolymer, this homopolymer has a photostability toward the incident wavelength throughout the film. The variables upon the film surface of the homopolymer have produced a porosity, which is due to the change in an atom volume of the molecular to promote the homopolymer performance toward the incident light over the film [9].

In the present study focused on PVC films modifying and characterized to derive modify PVC films with the organic group (amino group with a suitable aromatic aldehyde) to improve the optical properties such as absorption coefficient, reflectance, transmittance, skin depth, energy gap, refractive index, extinction coefficient, and Urbach energy for these modified compounds, and also stated the effect of surface morphology. The present study is a unique study, and to the best of our knowledge, no previous researchers did the same study or publish any research paper in this field until now by using these types of organic group films on the PVC surface, therefore the optical properties of the PVC will improve. It is worth mentioning, through the present study, the energy gap has been decreased to keep up the modified films without incorporates any nano-materials inside the PVC lattice and produce novel compounds that have the ability to absorb the incident light to be anti-reflective, for good use in high refractive lenses and photovoltaic cell applications.

2. Experimental work

2.1. Materials and apparatus

The materials used in the experiment have been bought from alfa caesar and sigma Aldrich companies without additional purification. The diffusion reflectance wavelength (A vantes DH-S-BAL-2048, UV-Visible Spectro-2048) was used to analyze and record the data for the incident wavelength range between (200-1300 nm), with step wavelength 2 nm. Scanning electron microscope S50 low vacuum (3 nm at 30 kV SE) was used to exhibit the microstructure and morphology of the pure and modifying surface. MEIJI equipped with INSTEC hot stage and central processor controller MK 1000 and connected with Lumenera color video camera by the strength of magnifies 20X also utilized to signifies the surface morphology.

2.2. PVC film Modification

An amino group with a suitable aromatic aldehyde (0.05 g) and polymer PVC (0.25 g) mixture with tetrahydrofuran (THF) 8 mL were refluxed for 5 h. The glass substrate has been washed with ethanol many times and then dried for 24 h at room temperature 25 °C. The solution of PVC has been poured above the glass substrate. The PVC modified films were synthesized by using the technique of evaporation at room temperature 25 °C. The thickness of PVC modified films was determined with utilized A Digital Vernier Caliper 2610A micrometer (Vogel GmbH, Kevelaer, Germany) to measure the thickness, which was found to be 40 μm. All reactions between the PVC and organic group stated in figure (1), which exhibit the structure as a chemical scheme of PVC lattice to pertain organic group within its structure [7, 54].

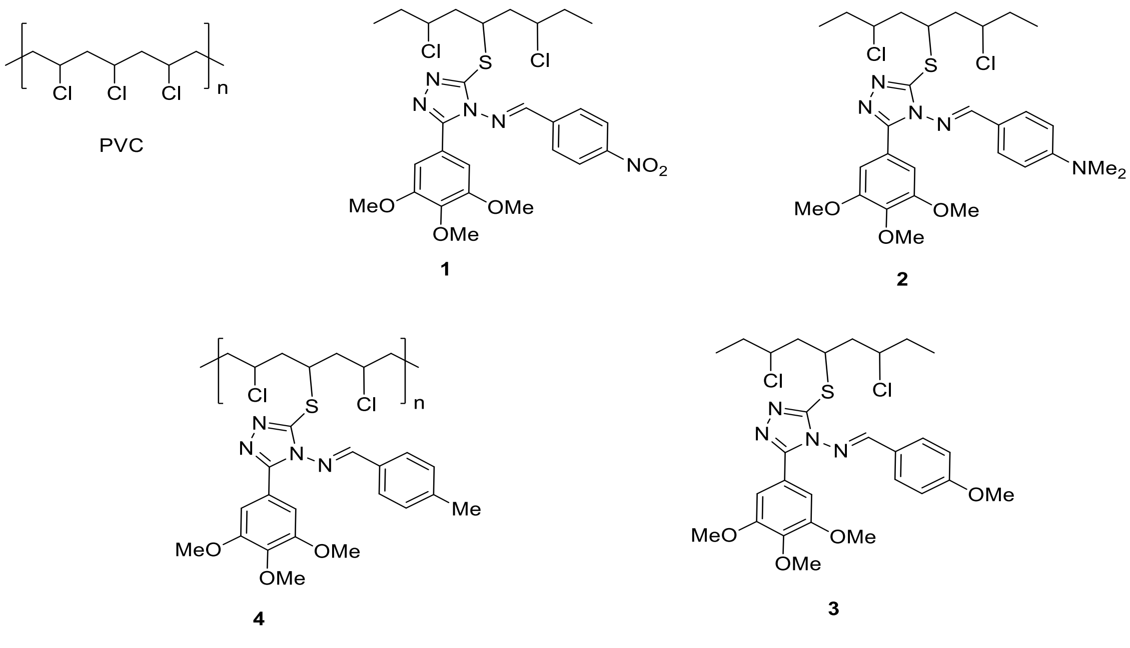

Figure (1) pure PVC and Modified films (1-4) scheme [7]

3. Results and Discussion

3.1. Reflectance test calculation of pure PVC and modified films

The reflectivity test is the percentage rate between the reflection of the wavelength through the surface coating film to the incident wavelength on it. Therefore, the reflectivity is represented as a result of the incident angle of the wavelength when particles strike the coating. Figure (2) shows reflectivity as a function for the wavelength of photon [11, 12].

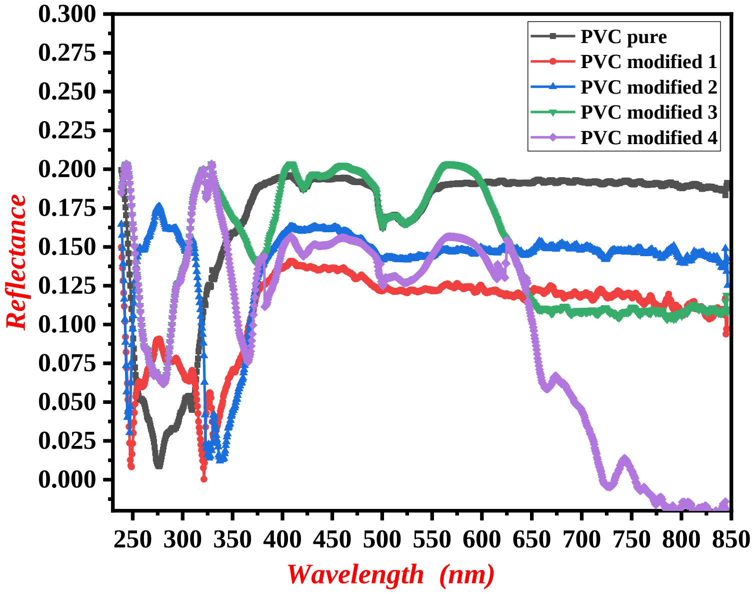

Figure (2) Reflectivity test for pure PVC and modified films (1-4) with a wavelength

It is obvious from figure (2) that the reflectance (*R*) of pure PVC and modified films (1-4) have gradation in reflectance (*R*), whereas the pure PVC has a high reflectance (*R*) and the PVC modified film (specimen number 4) has a low reflectance from the other specimens. This result has followed the topography of the surface and accompaniment surface roughness, which lead to a decrease in the reflectance (*R*) for the incident photon wavelength over the surface coating. The best compound is PVC modified film specimen number (4) has a low reflectance (*R*) value from the other compounds; its behavior is the same as the semiconductor [1]. Thereby, from the above results of reflectance, the value of absorptivity ranging between (85-100 %) as shown in figure (2). The surface topography was analyzed by utilizing scanning electron microscope (SEM) [55].

3.2. Absorption coefficient calculation of pure PVC and modified films

The absorption coefficient (α) is relied on the surface morphology in accordance with the reaction between the PVC and organic group. The spectrum of absorption for semi-crystalline compounds is dependent on the levels of electrons and how much contain energy in them. This synchronizes the vibrating of atoms when the incident wavelength strikes atoms, and accompanied this vibration losing or acquiring energy, the losing energy accompanied by moving the electrons from one level to another, and acquiring energy is due to the absorption energy [13,14]. Therefore, the variation in the spectral wavelength of the absorption coefficient (α) with wavelength for a pure PVC and modified films specimen number (1-4) demonstrates in figure (3).

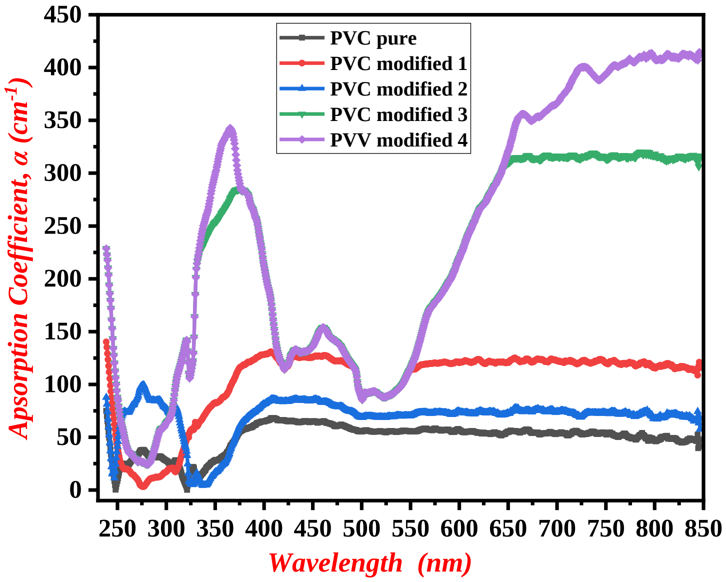

Figure (3) Absorption coefficient for pure PVC and modified films (1-4) with a wavelength

The data of absorbance can be used to calculate the absorption coefficient (α) from Beer lambert's equation [15, 16]:

$$\boldsymbol{\alpha} = \mathbf{2.303} * \frac{\boldsymbol{A}}{\boldsymbol{t}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, (α) the absorption coefficient in (cm^{-1}), (A) the value of absorbance, (t) coating thickness in (cm).

In figure (3) exhibits the absorption coefficient (α) of the pure PVC and modified films (1-4), pure PVC has a low value of absorption coefficient(α), whilst the PVC modified films (3 and 4) have a high absorption coefficient (α) compare with other samples. The absorption coefficient (α) magnitude is exhibited in figure (3), which is subjected to a variable such as a band edge region of semi-crystalline structure of the particles, whereas it is responsible for the value of absorption coefficient (α) when it is decreasing or increasing [17, 18]. From the results above, the best compound is PVC modified film number (4), which has a high value apposite a wavelength equal (λ=375 nm) under the UV region, and decline to a wavelength value between (λ= 400-525 nm), which considers the start value from the visible region and reaches up to the highest value from other compounds. This decrease due to the low homogeneity content of the coating through this region. The absorptivity values ranged between (85-100 %) and the improvement for this compound is proved that specimen number (4) become a semiconductor throughout the modification of PVC films [19, 20].

3.3. Skin depth of pure PVC and modified films

According to the high absorption of the PVC modified films must explain, in the semi-crystalline films, since the light fall over the coating is absorbed thoroughly, but this process depends on the angle when this angle is oblique some of the incident light is reflected from the film surface, and this will cause losing in the energy absorbed. There is another parameter called skin depth (x) is dependent on the wavelength energy (λ) that penetrates through the film thickness and the extinction coefficient (k). Skin depth (x) was computed from the photon wavelength (λ) and the absorbance coefficient (α) through this equation [21]:

$$\boldsymbol{x} = \frac{\boldsymbol{\lambda}}{\mathbf{2}\boldsymbol{\pi k}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where, (x) is the skin depth in (nm), (λ) is the wavelength in (nm), (k) is the extinction coefficient.

Therefore, figure (4) exhibits the variation of skin depth (x) with the photon wavelength, skin depth (x) is regarded as measuring the blackness of the films and this will lead to lowering the transparency of the material. Figure (4) shows the skin depth (x) decreasing with the wavelength for all the specimens and become zero at a wavelength value (λ=400 nm). When the value of skin depth (x) becomes zero, there is energy cut off in corresponding wavelength to this value and is called ($\lambda_{\text{cut-off}}$), through this region, the absorbance fade, and skin depth (x) value will increase dramatically [22]. After then, the peak value of skin depth (x) decreases to zero, which leads to the highest absorption in the films will be occurred gradually. Thereby, from figure (4) pure PVC film has a high value of skin depth (x) lead to a decrease in thickness, and has a low absorption from the other specimens. But, the other compounds of PVC modified films number (3 and 4) except PVC modified films number (1 and 2) have a low value of skin depth (x) through the region of the wavelength confined between (200-400 nm) which is illustrated by a small figure inside the original figure (4), because these films have the highest value of absorbance [12, 23]. After then, when the value of wavelength is greater than ($\lambda_{\text{cut-off}}$) (>400 nm) the skin depth fade (x=0) and the PVC modified films number (1 and 2) have the highest value of absorbance. So, at low energies, skin depth (x) is increased when reducing the amplitude of the diffused electromagnetic waves. Further, this prove that these films are semi-crystalline and semiconductor [24, 26].

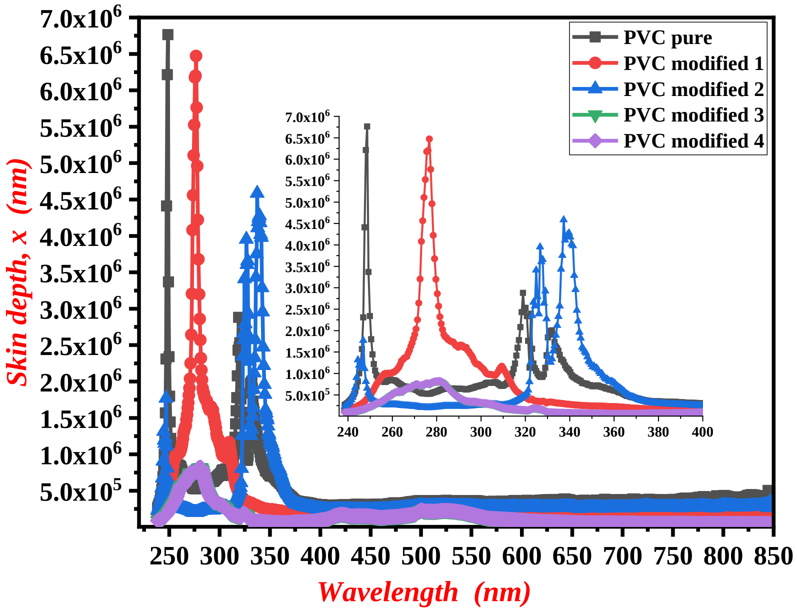

Figure (4) Skin depth for pure PVC and modified films (1-4) with a wavelength

3.4. Transmittance of pure PVC and modified films

Generally, the optical properties of any material relied on the interrelation between the nature of the material and the incident photon wavelength, therefore, all the optical parameters in the current study computed in terms of reflectance (R), and transmittance (T) for the samples. Further, as noticeable in the exhibit figure (5), which is shown the transmittance (T)variation with the wavelength [27].

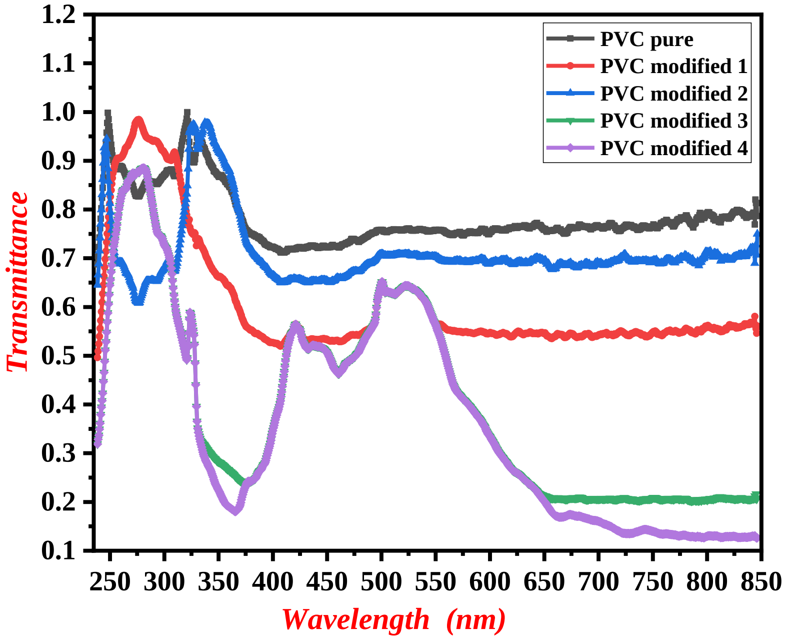

Figure (5) Transmittance for pure PVC and modified films (1-4) with a wavelength

In addition, when the percentages of organic group is increase, the value of the transmittance (T) already comparatively will be lower, as shown from curves figure (5). This should be ascribed to the organic group concentration in the compound, which stated a high absorption value through the surface of the film coating. So, figure (5) shows the compounds of pure PVC film and modified films specimen number(1 and 2) have a high transmittance (*T*), which is differs from the other two compounds PVC modified specimen number (3 and 4), which have a lower transmittance (*T*), whereas, these two samples have a lower value of (*T*=0.15), which begin from the wavelength (λ=360 nm), and then rises up to the value of (*T*=0.65), then declines to a lower value of (*T*=0.15) at a wavelength (λ=660 nm) and continuously in decreasing until reaches to (*T*=0.1). The fluctuation through a confined region wavelength ranged (360-660 nm) is ascribed-homogeneity of the mixing for two compounds between polymer PVC with organic compounds, this will influence the defect in the structure of these compounds which give this result [28]. This will confirm that the surfaces of the PVC modified films have been deposited of good quality coating, and they behave like a semiconductor or, in another meaning as the semi-crystalline compound.

3.5. Refractive index of pure PVC and modified films

A refractive index (*n*) is one of the optical properties parameters that was computed from reflectance (*R*) and extinction factor (*k*) by using the following equation [29]:

$$\boldsymbol{n} = \left[\frac{\boldsymbol{1+R}}{\boldsymbol{1-R}}\right] + \sqrt{\frac{\boldsymbol{4R}}{(\boldsymbol{1-R})^{2}} - \boldsymbol{k}^{2}} \text{.................. (3)}$$

Where (*n*) is the refractive index, (*R*) is the reflectivity and (*k*) is the extinction factor.

The refractive index demeanor (*n*) has strong high absorption for the compounds that used in refractive lenses and photovoltaic cell applications [19]. This is dependent on the incident angle of the wavelength that strikes the film surface, while the refractive index has a relation between reflectance (*R*) and the extinction factor (*k*) so that the graph will be a hybrid of the above two parameters. But the values of the reflectivity are higher than the extinction factor values; therefore, the reflectivity values dominated, and the graph will be similar to the graph of the reflectance (*R*) as shown in figure (6), which is illustrating the variation between refractive index data and the wavelength [12].

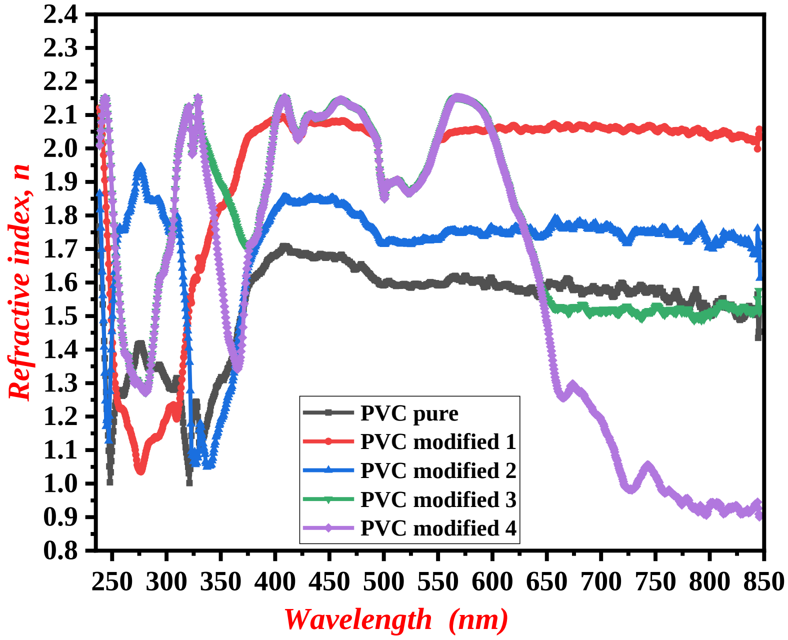

Figure (6) Refractive index for pure PVC and modified films (1-4) with a wavelength

It can be exhibited from figure (6) that the greatest value of the refractive index (n=2.15) at a region of the longer wavelength (λ=600 nm), as well at the range of wavelength (λ>600 nm), then decline of the refractive index is sharply and arriving at a low value of (n=0.9) at wavelength (λ≥800 nm) for the PVC modified film number (4), this decline happens due to the defect of the numbers of particles that have unsaturated bonds constructed through a deposition. After then, the *n* value remains unchanged for the entire wavelength. Also, the demeanors of the refractive index for pure PVC film and modified films numbers (1, 2, and 3) are similar started to oscillating in the region of the wavelength confined between (200-400 nm), and the *n* values for the above curves are unchanged along the entire wavelength, by owing dispersion normally; therefore the best compound is PVC modified film (4) has a high refractive index value from other compounds [19].

3. 6. Extinction factor of pure PVC and modified films

The extinction factor of solid materials is associated with the semi-crystalline structure of the particles. The waves of semi-crystalline material are dispersed on the surface of particles when the agglomeration occurred so that the waves will be propagated randomly inward grain borders for solid materials; for this reason, the value of extinction factor (*k*) small, whilst the value of *k* in amorphous structure is high. Many causes of scattering irregular internally will lead to an increase in absorption coefficient when the accumulation of particles is decreased of amorphous material, the extinction coefficient (*k*) increases, whilst when accumulation increases of semi-crystalline materials, there is a decrease in the extinction coefficient (*k*). The extinction coefficient (*k*) is calculated from the data of the absorption coefficient and wavelength as shown in the equation below [30, 31]:

$$\boldsymbol{k = \frac{\alpha\lambda}{4\pi}} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where, (α) the absorption coefficient in (cm^{-1}), (λ) is the wavelength in (cm).

The extinction factor (*k*) for all compounds are shown in figure (7), It is obvious that the values of extinction factor are small, this is proved that all compounds are semi-crystalline. The best compound is PVC modified film number (4), from the other compounds.

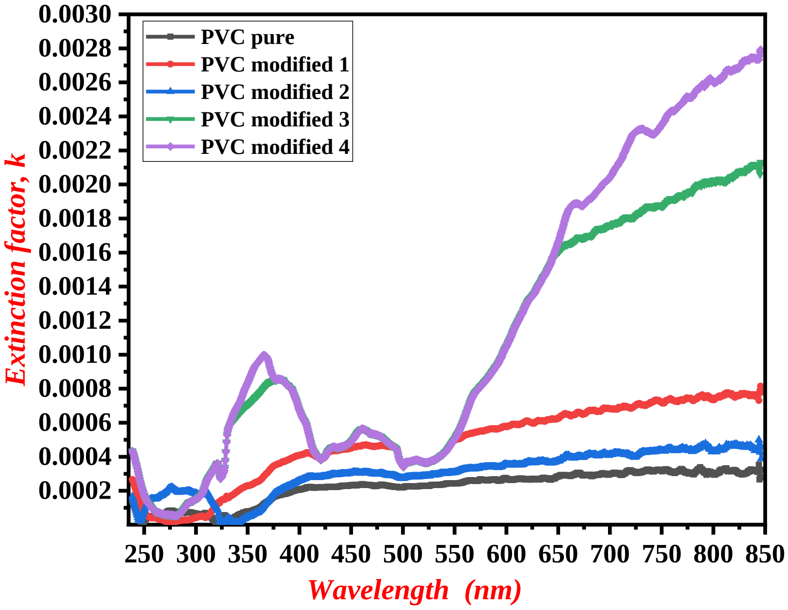

Figure (7) Extinction factor for pure PVC and modified films (1-4) with a wavelength

3.7. Real and imaginary of dielectric constant of pure PVC and modified films

The wave diffusion is dependent on the dielectric constant (Ɛ), which defined as the amount of the dislodge net current with the changeable time for solid material and describes the optical properties that depend on the light wavelength. The dielectric constant is specified and can be classified into two parts: real and imaginary which have been determined by the current relation [32]: $[(\mathcal{E}) = \boldsymbol{\mathcal{E}_1(\omega) + i\,\mathcal{E}_2(\omega)}]$ ………… (5)

The above factors rely on (*n*) and (*k*) magnitudes and computed from the next equations [33, 34]:

$$\begin{bmatrix} \boldsymbol{\varepsilon_1 = n^2 - k^2} \\ \boldsymbol{\varepsilon_2 = 2nk} \end{bmatrix} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (6)$$

Where the magnitudes of ($\mathcal{E}_1$) and ($\mathcal{E}_2$) depend on the light wavelength.

The dielectric constant of the compounds of pure PVC film and modified films specimen numbers (1, 2, 3, and 4) with their parts $\mathcal{E}_1$ and $\mathcal{E}_2$ were computed at various worth of wavelengths and exhibits in figure (8 and 9). The real part ($\mathcal{E}_1$) curves shown in figure (8) is associated with the refractive index (*n*) and the extinction factor (*k*), as demonstrated in equation (6). Thus, the data of the present study for *n* is greater than *k* and will be had the same shape of the refractive index (*n*), whereas shown in figure (8) with a slightly differ in the subtraction process of the equation (6) [35, 36].

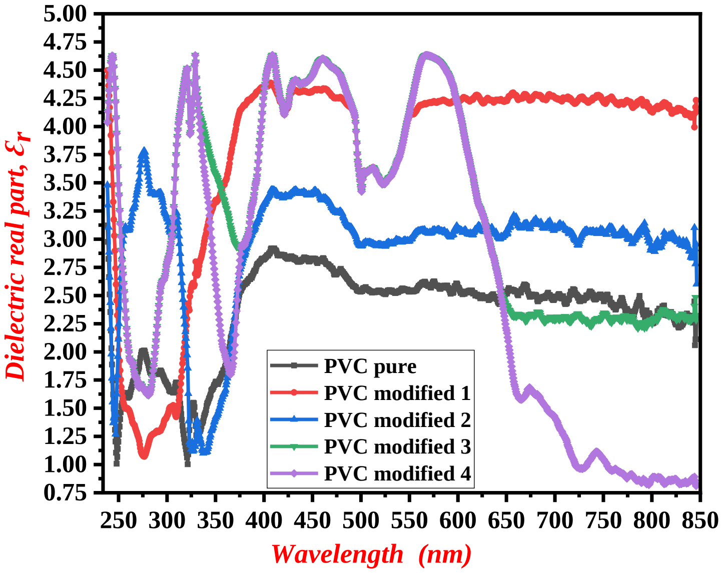

Figure (8) Dielectric real part for pure PVC and modified films (1-4) with a wavelength

It may be seen from the figure (8) that the greatest value of $\mathcal{E}_1$ is (4.625) at a region of wavelength (λ=600 nm), after audit for (λ>600nm), $\mathcal{E}_1$ declines sharply and arrives at a small value which is (0.75) at ($\lambda \geq$800nm) of the PVC modified film (4), so the $\mathcal{E}_1$ value remains constant along axis of wavelength (λ). Also, for pure PVC film and modified films (1, 2, and 3) are similar and fluctuating in the region of the λ confined between (200-400 nm), and continues constant along the entire λ, this result owing to dispersion in a mixture; therefore the best compound is PVC modified number (4) which has a high $\mathcal{E}_1$ value from other compounds [11, 12].

Figure (9) exhibits the imaginary part ($\mathcal{E}_2$) of the dielectric constant associated with equation (6), which demonstrated the multiplying process of (n) and (k). thus, magnitude of (k) is a low value from (n), and its effect appeared in multiplying, which made the shape of the graph similar to the shape of extinction factor graph, all this shown in figure (9).

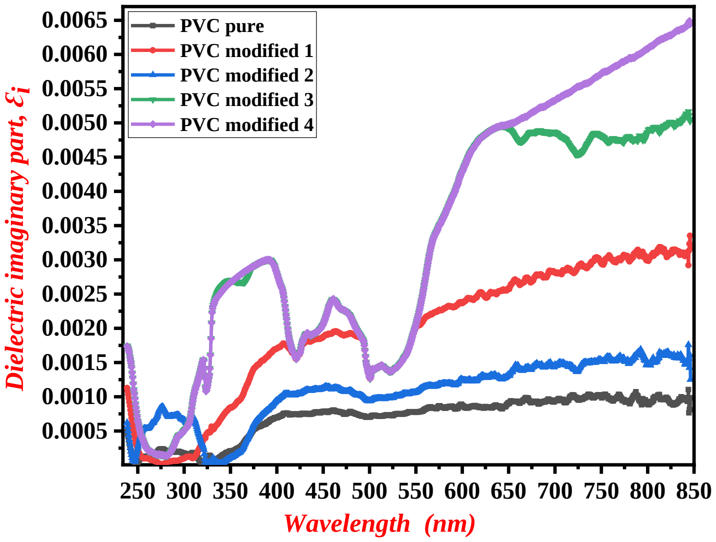

Figure (9) Dielectric imaginary part for pure PVC and modified films (1-4) with a wavelength

It is obvious from figure (9) that the value of $\mathcal{E}_2$ of PVC modified films (3 and 4) have the highest value than the other curves. Still, there is a fluctuating occurs in the region confined for λ (400-600 nm), and this due to irregular dispersion of the mixture, so the other curves have low values of $\mathcal{E}_2$ and continues increases slightly along the axes of wavelength (λ). The best compound is PVC modified film number (4) have a high conductivity from the other curves [19].

3.8. Optical conductivity of pure PVC and modified films

When electrons are moved from the valence to the conduction bands through an energy gap gives the conductance to the material. This conductance associated with the absorbance of the particle from the incident light wavelength, which strikes the surface coating of the samples. Therefore, these particles have the ability for acceleration through the electrical created field between them. This conductance is called optical conductivity, which contains two variables as absorption coefficient (α) and refractive index (n) for the samples and can be calculated from the equation below [20]:

$$\boldsymbol{\sigma} = \frac{\boldsymbol{\alpha n c}}{\boldsymbol{4\pi}} \dots\dots\dots\dots\dots\dots\dots\dots \text{(7)}$$

Where (Ϭ) is the optical conductivity (Ω.cm^{-1}), (α) is the absorbance coefficient (cm^{-1}), (n) is the refractive index, and (c) is the velocity of light (3x1010 cm/s).

Thereby, the electrons missing from the valence band through the activation and transfer to the conduction band can create holes, which regarded as the basic rule of conductivity. When the thickness of the film is increased, the optical conductivity for semi-crystalline or semiconductor material increases; therefore, the optical conductivity of the resulting data is demonstrated in figure (10) [11, 29].

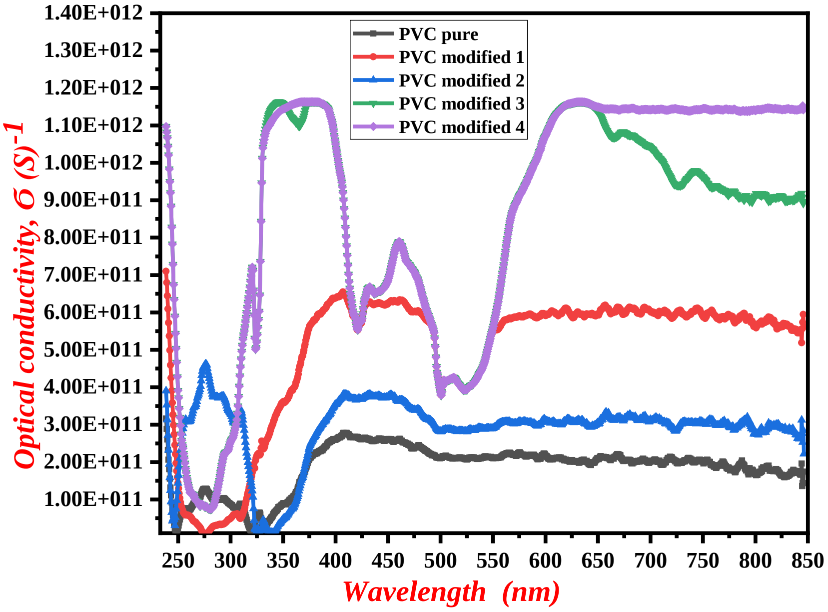

Figure (10) Optical conductivity for pure PVC and modified films (1-4) with a wavelength

It is obvious from the figure (10), the relation between the optical conductivity with the wavelength, exhibits the nature of PVC modified films (3 and 4), have the highest value than the other curves, but there is a fluctuating occurs in the region confined for wavelength (λ) (400-600 nm), and this due to irregular dispersion of the mixture, so, the other curves have low values of $\mathcal{E}_2$ and continues increases slightly along the axes of wavelength (λ). The best compound is PVC modified film number (4) have a high conductivity from the other curves [37].

3. 9. Optical energy gap of pure PVC and modified films

Tauc's function is proposed to estimate the optical band gap for the high absorption coefficient as exhibits in equation (8) [12]:

$$\boldsymbol{\alpha h\nu = A\ (h\nu - E_g)^n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (8)$$

Where (*A*) is a constant connection with the semiconductor order, (*Eg*) is the energy gap of the compounds, and (n) is the power of the allowed transition (n=0.5 for indirect transition and n=2 for direct transition) [11, 18].

The direct line segment has been extrapolated from the chart demonstrated in figures (11 and 12) to zero value of the x-axis to give the identical *Eg* values.

It is gotten the energy gap values from the figure (11) of electronic allowed transition for the pure PVC films and modified films specimens number (1, 2, 3, and 4). The energy gap is dependent on the deposition of PVC thin films compounds because a deposition is a fundamental step for the film; if the deposition of organic compounds homogenous distributed within PVC lattice, a good value of energy gap will be achieved. Therefore, the energy gap decreases with adding the organic compounds to PVC and through the crystalline structure, It is seen a two energy gap of PVC modified films specimens number (2, 3, and 4), and their values decreased from (5.1 to 2.9 eV), from the main value of pure PVC film which equal (5.1 eV) as shown in figure (11). The two values of the energy gap that appear in PVC modified films specimens number (2, 3, and 4) are associated with blending and resulting in defects in modified films because many atoms have unsaturated bonds that produce with deposition [38, 54].

Subsequently, the energy gap values for the direct allowed transition are listed in the table (1).

Table (1) Energy gap (*Eg*) of direct transition for pure PVC and modified films (1-4)

Eg of pure PVC (eV)	*Eg* of PVC modified 1 (eV)	*Eg* of PVC modified 2 (eV)	*Eg* of PVC modified 3 (eV)	*Eg* PVC of modified 4 (eV)
5.1	5.0	3.8, 5.1	2.9, 4.95	2.9, 4.95

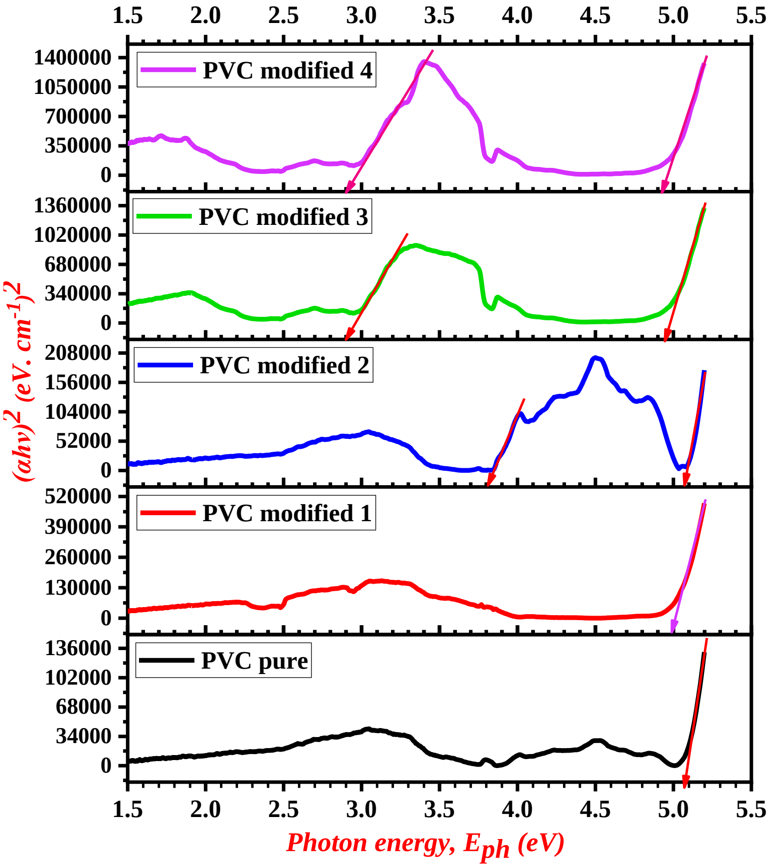

Figure (11) Energy gap of direct transition for pure PVC and modified films (1-4) with photon energy

Also, it is seen from figure (12) many values of energy gap for indirect transition; it decreases from (5 to 2.8 eV) when adding an organic group to the PVC modified films as seen in specimens number (2, 3, and 4) as shown in figure (12). In this figure, there are two values of energy gap that appeared in these modified films, but the pure PVC film has an energy gap value equal to (5 eV). The best values of indirect energy gap obtained belong to a fine blend of regular exploited organic compounds within PVC structure. Thus, values of the energy gap for the indirect allowed transition are listed in the table (2) [39, 54].

Table (2) Energy gap (*Eg*) of indirect transition for pure PVC and modified films (1-4)

Eg of pure PVC (eV)	*Eg* of PVC modified 1 (eV)	*Eg* of PVC modified 2 (eV)	*Eg* of PVC modified 3 (eV)	*Eg* PVC of modified 4 (eV)
5.0	4.7	3.8, 4.95	2.8, 4.7	2.8, 4.7

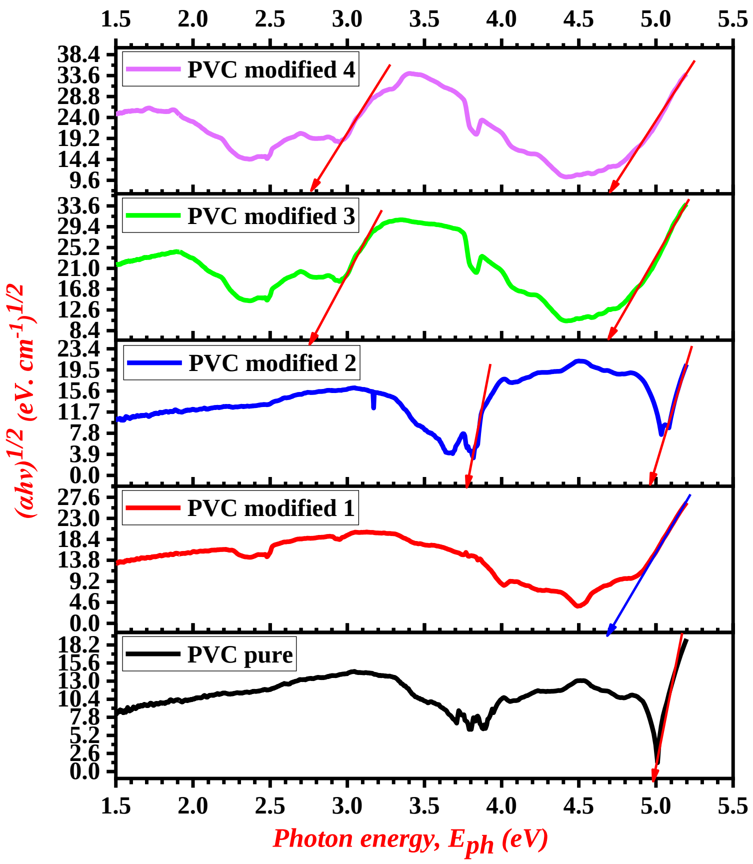

Figure (12) Energy gap of indirect transition for pure PVC and modified films (1-4) with photon energy

3. 10. Urbach energy of pure PVC and modified films

Band tail size is the one of the lost data for a long interval, it is associated with the atoms in optical band edges. Through, the field of optical edges there is a relevance for the absorption coefficient (α) and the photon energy (hv), is called urbach energy. Equation (9 and 10) determines this relation [40, 41]:

$$\alpha = \alpha_o exp\frac{hv}{E_u} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where, (α_o) is a constant, and (E_u) is the Urbach energy.

In addition, by picking the logarithms for the two side of equation (9), and then can get a straight line as shown in equation (10) [11]:

$$ln\ \alpha = ln\ \alpha_o + \frac{hv}{E_u} \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

A band tail width (E_u) of the absorption edge, and in figure (13) is exhibited the demeanor of Ln (α) opposite to the photon energy (hv). The data obtained of a band tail are listed in table (1). The (E_u) values shows in figure (13), it is clear the values decrease from -5.779 to -1.905 for pure PVC and modified films. This decrease ascribed to the regular mixing for the compounds of pure PVC and modified films (1-4) with the organic group, which lead to an increase in turbulent defects and atoms transition through the structure binds, will create a torrent of holes in the valence band, while the conduction band will be full the electrons. Therefore, this proves that the compounds of PVC modified films (1-4) are semi-crystalline and semiconductor [42-44].

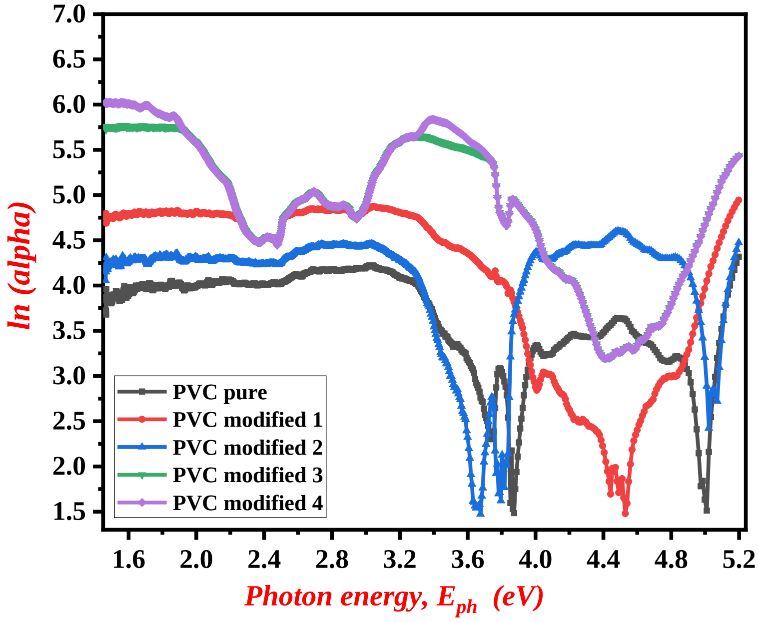

Figure (13) Urbach energy for pure PVC and modified films (1-4) with photon energy

Defects and disorders that happen in the bonds of structure lead to increase (E_u) bandwidth, this will cause the motion of electrons within the structure and become nearby the level band of connection. Therefore, these electrons are ready to cross the barrier and grant conductivity to the PVC modified films. Consequently, the values of urbach energy are listed in table (3) as exhibited in figure (13) [45, 56].

3.11. Higher frequencies of dielectric constant of pure PVC and modified films

The relation between the square refractive index and square wavelength for either solid material depended on Maxwell's equations, which deals with wave diffusion through the material and associated with the dielectric constant ($\mathcal{E}$) which stated the value of the current of displacement with various time of incident light wavelength on the practical domain [11, 21], The optical properties for solid materials can be characterized and dependent on the incident wavelength, the dielectric constant high frequency $\left(\frac{N}{m^*}\right)$, and the charge carrier content with the effective mass ($\mathcal{E}_\infty$) as shown in equation (11) [46]:

$$n^2 = \varepsilon_1 = \varepsilon_\infty - \frac{1}{4\pi^2\varepsilon_0}\left(\frac{e^2}{c^2}\right)\frac{N}{m^*}\lambda^2 \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where, ($\mathcal{E}_\infty$)is the dielectric constant with high frequency, $\left(\frac{N}{m^*}\right)$ is the charge carrier content to the effective mass, (e) is the basic charge of the electron,(c) is the speed of light has a constant value, and (ε_0) is the magnitude of electrical permittivity for air [47].

It is seen in figure (14) the graph of $n^2$and λ^2,the values of $\left(\frac{N}{m^*}\right)$ and (ε_0) can be determined by taking the slope of all curves for pure PVC and modified films and then by intercepting them with the y axis when wavelength λ^2 equal zero. All these values are illustrated in table (3).Accordingly, to the equation (11) the slope $\left[\frac{1}{4\pi^2\mathcal{E}_0}\left(\frac{e^2}{c^2}\right)\frac{N}{m^*}\right]$is acquired from figure (14)to gain the values which is listed in table (3). After computing the results, it was found that the values of $\left(\frac{N}{m^*}\right)$ increased from (2.2046x10^{61} to 18.3941x 10^{61} (kg. m^3)$^{-1}$) and (ε_0) increased from (2.147 to 4.387) when the organic compound added, then, the demeanor of the curves in figure (14) are coincides to the demeanor of the refractive index in above [48, 57].

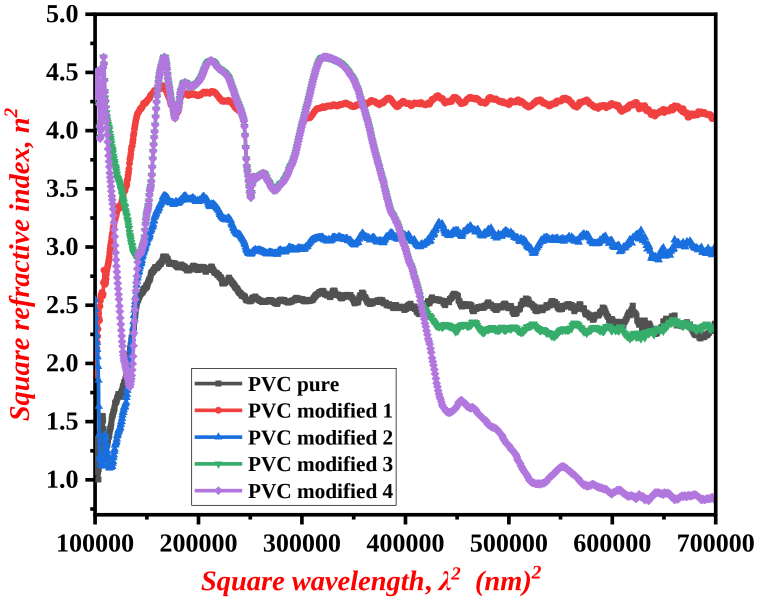

Figure (14) n^2 with $\lambda^2$for pure PVC and modified films (1-4)

In addition, all the results that found are similar to the behavior of semiconductor, the results of the present study are a good agreement with semi-crystalline semiconductor. the dielectric constant with high frequency is regarded as a crucial factor to design many instruments and printed sheet of electronic circuit [49–52].

3.12. Model of Wemple Di-Domenico of pure PVC and modified films

Study the energies of the effective single oscillator (E_o) and the scattering energy (E_d) are very important. Therefore, there is a relation between these energies and the refractive index with photon energy as exhibited in equation (12) and its mentioned as Wemple-DiDomenico [51]:

$$(\boldsymbol{n^2-1}) = \frac{\boldsymbol{E_d E_o}}{[\boldsymbol{E_o}^{\boldsymbol{2}} - (\boldsymbol{h\nu})^{\boldsymbol{2}}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}$$

Reorganize the above equation, after then becomes:

$$(\boldsymbol{n^2-1})^{-\boldsymbol{1}} = \frac{\boldsymbol{E_o}}{\boldsymbol{E_d}} - \frac{(\boldsymbol{h\nu})^{\boldsymbol{2}}}{\boldsymbol{E_d E_o}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(12)}$$

Reciprocal of square refractive index $[(n^2-1)^{-1}]$ with $[(h\nu)^2]$ have been plotted in figure (15) to compute the magnitude of the ratio for these energies $(\frac{\boldsymbol{E_o}}{\boldsymbol{E_d}})$ through interrupts the y axis and produce the slope that gives the value of $(\frac{1}{\mathrm{EoEd}})$. After then, the values of (E_o) and (E_d) can be obtained by the calculations [51, 56, 57].

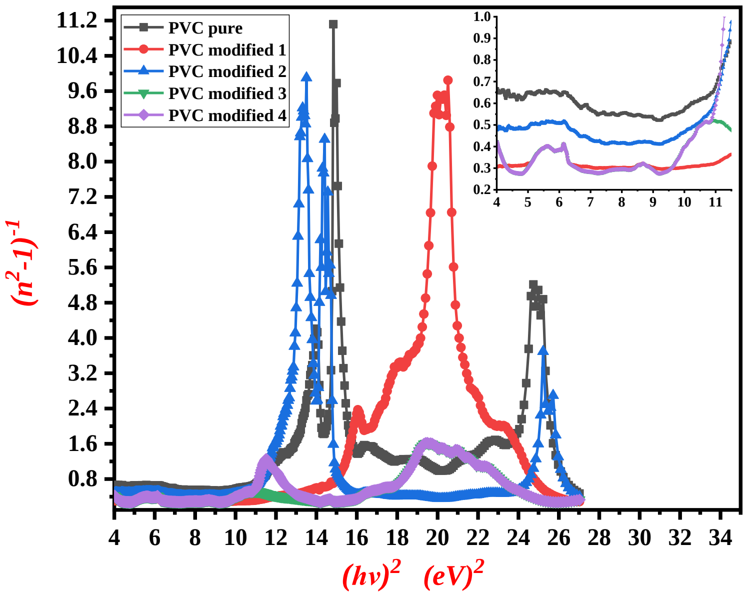

Figure (15) Reciprocal square refractive index $(n^2-1)^{-1}$ versus $(h\nu)^2$ for pure PVC and modified films (1-4)

The values of the oscillator energy (E_o) decreases from (20.888 to 0.8344 eV) and dispersion energy (E_d) also decreases from (38.61 to 1.393 eV) and all these values are listed in table (3), this decrease belong to the defects in the structure of the particles. As clear in the curves figure (15), the defects in shape are associated with the precipitation because there are a huge number of atoms that have their bonds unsaturated and exhibited with precipitation. Therefore, it has been investigated to draw a small curve inside the original curve to show the original behavior of the films; these defects cause a disorder to the electrons that will cause this case [52, 56].

3. 13. Tangent loss of dielectric constant of pure PVC and modified films

The tangent loss of dielectric constant is a principal parameter for the opto-electrical. the loss means that the energy of electron dissipated throughout the moving of the charges in the field of electromagnetic. The tangent loss of material is determined from the real and imaginary factors, and called the ratio between the imaginary part upon the real part for the dielectric constant, therefore it is computed from equation (13) as illustrated bellow [11]:

$$\boldsymbol{\tan\delta = \frac{\varepsilon_2}{\varepsilon_1}} \ldots\ldots\ldots\ldots\ldots\ldots\ (13)$$

It can see from figure (16) the tangent loss variation versus incident wavelength for all the studied samples of pure PVC and modified films. The values of the real dielectric constant are more significant than the values of the imaginary dielectric constant, resulting a low value of the tangent loss [52]. Whereas, in figure (16), the higher value is equal 0.00625. Thereby, the above results confirm that there is an influence on the free electrons in the structure of particles by the incident wavelength; this leads to decelerate and curb the speed of the distribution of the electromagnetic waves that effected upon the free electrons. Also, there is an important point to confirm when the imaginary dielectric constant has great values, and this will lead to a high loss in *tan δ* [52].

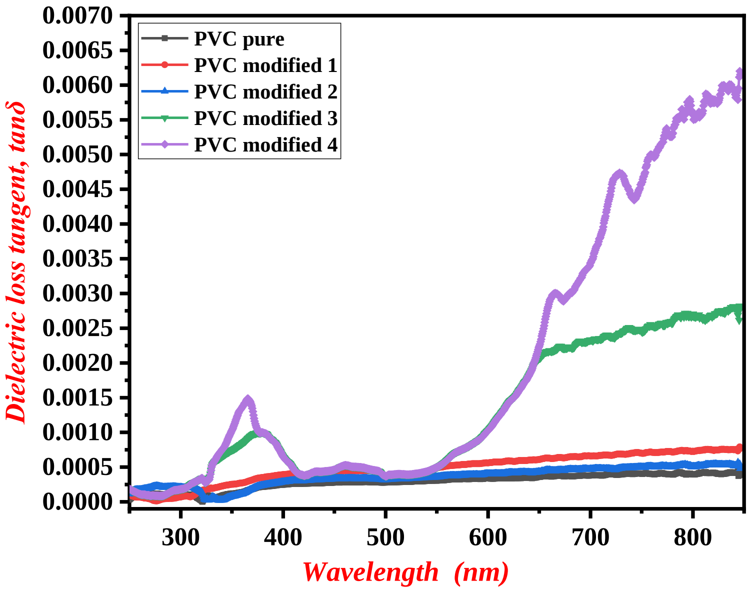

Figure (16) Dielectric tangent loss for pure PVC and modified films (1-4) with a wavelength

It is obvious from figure (16), the tangent loss of dielectric constant is increased. It will reach a higher value in the region of $\tan \delta \geq 600$ nm, then, in the low value of wavelength region of $\tan \delta \leq 600$ nm, which has a lower value. Therefore, the tangent loss of dielectric constant of PVC modified films specimens number (3 and 4) continue increasing to high values, but in the case of pure PVC and modified film specimens number (1 and 2) have lower values of $\tan\delta$ and continue to increase slightly along the axis of wavelength [52, 57].

Thereby, all the above results can be tabulated in the table3 below for all parameters of the optical properties, direct and indirect allowed transition(Eg), constant(α_o), Urbach energy (Eu), single oscillator energy ($\boldsymbol{E_o}$)**,**the dispersion energy **(**$\boldsymbol{E_d}$**)**,the carrier concentricity for every effective mass $\left(\frac{\boldsymbol{N}}{\boldsymbol{m^*}}\right)$, and the high-frequency dielectric constant values ($\mathcal{E}_\infty$), as illustrated in table (3) [19]:

Table (3) exhibited all values of the optical properties of the present work.

No.	Essential parameters	Pure PVC	PVC modified 1	PVC modified 2	PVC modified 3	PVC modified 4
1	Direct allowed transition of (Eg) eV	5.1	5.0	3.8, 5.1	2.9, 4.95	2.9, 4.95
2	Indirect allowed transition of (Eg) eV	5.0	4.7	3.8, 4.95	2.8, 4.7	2.8, 4.7
3	Urbach energy (Eu) eV	3.778	1.961	5.779	2.149	1.905
4	($\boldsymbol{\alpha_o}$) constant **(**cm^{-1}**)**	91.762	331.756	99.803	595.737	750.846
5	energy of the dispersion ($\boldsymbol{E_d}$) eV	6.024	6.293	2.297	38.61	1.393
6	unique oscillator energy ($\boldsymbol{E_o}$) **eV**	2.335	1.359	0.834	20.888	3.587
7	Dielectric constant high-frequency values ($\mathcal{E}_\infty$)	2.147	2.874	2.762	4.061	4.387
8	Carrier concentricity per the effective mass $\left(\frac{\boldsymbol{N}}{\boldsymbol{m^*}}\right)$ x 10^{61}(m^3. Kg)$^{-1}$	2.509	10.021	2.205	9.510	18.394

4. Surface morphology of the pure PVC and modified films

The surface morphology was examined by SEM to signifies the organic compounds scattered in polymer PVC lattice. It is clear from scanning electron microscope examination that the organic compounds will increase the surface area of poly(vinyl chloride) (PVC) films compare with pure PVC. On the other hand, when the concentration of organic compounds increases, that means the number of particles on the surface of poly(vinyl chloride) increasing. In other words, the number of surface atoms for modified films increase. As a result, the optical properties of the coating surface will be improved, as explained previously. The optical microscope and scanning electron microscope photographs figure (17-a and 17-b) confirm the distribution and the concentration of the organic particles [52].

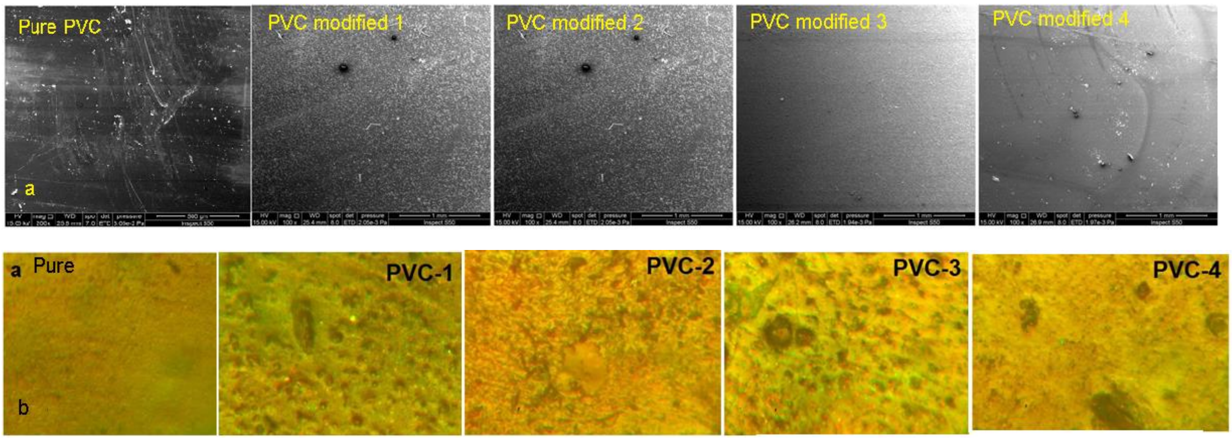

Figure (17) SEM images for pure PVC and modified films (1-4) with a wavelength

Conclusion

Semiconductor semi-crystalline of pure PVC and modified films have been synthesized by using the casting method. The optical properties have been investigated by applying the spectra of UV-Visible for pure PVC and modified films in the wavelengths range (200–1000 nm). The other parameters of extinction factor (k), Urbach energy (Eu), and skin depth (x) have been computed from the values of absorption coefficient (α), which determined from data of wavelengths. The energy gap (Eg) of direct and indirect allowed transitions has been calculated from Tauc's equation by utilizing the values of absorption coefficient (α), which associated with Tauc's equation for pure PVC and modified films.

It was clear, from the graphs of direct energy gap decrease from 5.1 eV to 2.9 eV, while for the indirect energy gap decreased 5.0 eV to 2.8 eV. Moreover, it is possible to compute the values of extinction factor (k) by using the data of wavelength and the absorption coefficient. In addition, the values of Urbach energy also decreased when adding the organic compounds to the polymer PVC content. Thereby, all the gained results were discussed according to the scientific foundations of the optical theories. The dispersion energy $(\boldsymbol{E_d})$ and single oscillator energy$(\boldsymbol{E_o})$**,** were calculated depending on the Wemple-Di-Domenico prototype for all pure PVC and modified films which improve by organic compounds. By inserting the data of the refractive index (n) in the equations, which used to calculate many parameters such as real (ε_1), imaginary (ε_2), the charge carrier for every effective mass $\left(\frac{\boldsymbol{N}}{\boldsymbol{m}^*}\right)$, and high-frequency (ε_∞) of dielectric constants. The semi-crystalline films will be utilized in several fields of opto-electronics as: microelectronic applications, transistors, and photovoltaic solar cells with low rate to use in spectroscopic properties.

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